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Lithium-Containing Composite Oxide and Nonaqueous Secondary Cell Made of the Same

[Translated from Japanese]

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Translation Requested by: Kevin Eberman 3M

Translation Provided by: Yoko and Bob Jasper
Japanese Language Services
16 Oakridge Drive
White Bear Lake, MN 55110

(651) 426-3017 Fax (651) 426-8483
e-mail: bjasper@attbi.com

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[Inventor]

[Address or Location] Hitachi Maxell Co., Ltd.

1-1-88 Ushitora, Ibaragi-shi

Osaka-fu

[Name] Atsushi Ueda

[Inventor]

[Address or Location] Hitachi Maxell Co., Ltd.

1-1-88 Ushitora, Ibaragi-shi

Osaka-fu

[Name] Kazutaka Uchitomi

[Inventor]

[Address or Location] Hitachi Maxell Co., Ltd.

1-1-88 Ushitora, Ibaragi-shi

Osaka-fu

[Name] Shigeo Aoyama

[Patent Applicant]

[Identification No.] 00005810

[Surname or Name] Hitachi Maxell Co., Ltd.

[Representative] Norio Akai

[Agents]

[Identification No.] 100080193

[Patent Attorney]

[Surname or Name] Yasuaki Sugiura

[Telephone No.] 0297-20-5127

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[Title of Invention] Lithium-Containing Composite Oxide and Nonaqueous Secondary Cell Made of the Same

[Claims of Invention]

[Claim 1] A lithium-containing composite oxide characterized by the fact that the composite oxide has a composition indicated by the general formula $Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$

[Wherein, $0 \leq x \leq 0.05$, $-0.05 \leq x+\alpha \leq 0.05$, and $0 \leq y \leq 0.4$, and $-0.1 \leq \delta \leq 0.1$ (provided that $0 \leq y \leq 0.2$) or $-0.24 \leq \delta \leq 0.24$ (provided that $0.2 < y \leq 0.4$), and M is one or more types of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn], and is produced by baking a composite compound containing at least Ni and Mn as structural elements and an Li compound.

[Claim 2] A lithium-containing composite oxide characterized by the fact that the composite oxide has the composition indicated by the general formula $Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$

[Wherein, $0 \leq x \leq 0.05$, $-0.05 \leq x+\alpha \leq 0.05$, and $0 \leq y \leq 0.4$, and $-0.1 \leq$ delta ≤ 0.1 (provided that $0 \leq y \leq 0.2$) or $-0.24 \leq$ delta ≤ 0.24 (provided that $0.2 < y \leq 0.4$), and M is one or more types of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn], and having diffraction peaks with an angle of diffraction 2θ at around 18° and around 44° by X-ray diffraction measurement that utilizes $CuK\alpha$ ray, and having two diffraction peaks at 63° to 66°, and furthermore, the ratio of the integrated intensity of the aforementioned diffraction peaks at around 18° I_{18}, and the integrated intensity of the diffraction peak at around 44° I_{44}, I_{44}/I_{18}, and difference of the diffraction angle 2θ of the two diffraction peaks exists at 63° to 66°, θa, are either $0.9 \leq I_{44}/I_{18} \leq 1.2$ and $0.3° \leq \theta a \leq 0.6°$ (provided that $0 \leq y \leq 0.2$) or $0.7 < I_{44}/I_{18} \leq 1$ and $0.55° \leq \theta a \leq 0.75°$ (provided that $0.2 < y \leq 0.4$), respectively.

[Claim 3] A lithium-containing composite oxide characterized by the fact that the composite oxide has the composition indicated by the general formula

$Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$

[Wherein, $0 \leq x \leq 0.05$, $-0.05 \leq x+\alpha \leq 0.05$, and $0 \leq y \leq 0.4$, and $-0.1 \leq \delta \leq 0.1$ (provided that $0 \leq y \leq 0.2$) or $-0.24 \leq \delta \leq 0.24$ (provided that $0.2 < y \leq 0.4$), and M is one or more type of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn], and has a true density in the range of 4.55 to 4.95 g/cm^3.

[Claim 4] The lithium-containing composite oxide described in claims 1 to 3 characterized by the fact that $-0.015 \leq x+\alpha \leq 0.015$.

[Claim 5] The lithium-containing composite oxide described in claims 1 to 4 characterized by the fact that the valance of Mn obtained by X-ray absorption spectral analysis is in the range of 3.3 to 4.

[Claim 6] A non-aqueous secondary cell characterized by the fact that the cell is made of a positive electrode that utilizes the lithium-containing composite oxide described in one of claims 1 to 5, a negative electrode, and a non-aqueous electrolyte. [Claim 7] The non-aqueous secondary cell described in claim 6 characterized by the fact that a separator with a thickness in the range of 5 to 20 μm is used.

[Detailed description of the invention]

[0001]

[Technical field of the invention]

The present invention pertains to a lithium-containing composite oxide used as positive electrode material, etc. of non-aqueous secondary cell, and to a non-aqueous secondary cell where the aforementioned lithium-containing composite oxide is used as a positive electrode.

[0002]

[Prior art]

In recent years, along with advancements in portable electronic machinery and equipment such as portable telephones and notebook type personal computers, and commercialization of electric cars in recent years, smaller, lighter weight and higher capacity secondary cells are required. Currently, as a high capacity secondary cell capable of meeting said requirements, non-aqueous secondary cells represented by lithium secondary cells that utilize $LiCoO_2$ as a positive electrode and carbon group material as a negative electrode are being commercialized. The aforementioned lithium secondary cell is gaining much attention as a power supply for portable electronic machinery and equipment from the standpoint of its high energy density and possible reduction in size as well as weight. The $LiCoO_2$ used as a positive electrode material for the above-mentioned lithium secondary cell is widely used as a suitable material for positive electrodes because of its ease of manufacturing and ease of handling. However, production of $LiCoO_2$ is done using the rare metal Co as a raw material, and scarcity of the natural resource is anticipated to become a serious problem in the future.

[0003]

Furthermore, the price of cobalt itself is high and price fluctuations are high as well, and development of a positive electrode material with a reasonable cost where a stable supply can be expected is desired.

[0004]

Thus, as the positive electrode material for a lithium secondary cell, high expectation is placed on lithium manganese oxide group materials in place of $LiCoO_2$. Among the materials, for lithium manganese oxides having a spinel-type structure, $Li_2Mn_4O_9$, $Li_4Mn_5O_{12}$, $LiMn_2O_4$, etc. can be mentioned, and in particular, research on $LiMn_2O_4$ is being actively carried out as it is capable of charge and discharge at a voltage range close to 4V against Li (Japanese Kokai [Unexamined] Patent Application No. Hei 6-76824, Japanese Kokai [Unexamined] Patent Application No. Hei 7-73883, Japanese Kokai [Unexamined] Patent Application No. Hei 7-

230802, Japanese Kokai [Unexamined] Patent Application No. Hei 7-245106, etc.).

[0005]

Incidentally, the theoretical discharge capacity of $LiCoO_2$ is 274 mAh/g, but when a deep charge and discharge is conducted, $LiCoO_2$ undergoes a phase change and the cycle life is affected; thus, the practical discharge capacity of the actual lithium secondary cell falls into a range of 125 to 140 mAh/g.

[0006]

On the other hand, the theoretical discharge capacity of $LiMn_2O_4$ is 148 mAh/g, but $LiMn_2O_4$ also undergoes a phase change during the course of charge and discharge as in the case of $LiCoO_2$, and when a carbon group material is used as the negative electrode material, the charge capacity when actually used as a cell is reduced to approximately 90 to 105 mAh/g due to the large irreversible capacity of the carbon group material. As this shows, an increase in cell capacity to a value greater than that when $LiCoO_2$ is used for the positive electrode active material is not possible when $LiMn_2O_4$ is used as a positive electrode active substance.

[0007]

Furthermore, the true density of $LiCoO_2$ is 4.9 to 5.1 g/cm^3, on the other hand, the true density of $LiMn_2O_4$ is a fairly low 4.0 to 4.2 g/cm^3, and when filling property as a positive electrode active material is taken into consideration, it is inconvenient from the standpoint of capacity.

[0008]

Furthermore, in a lithium secondary cell using $LiMn_2O_4$ as a positive electrode active material, the cycle characteristic is inferior in comparison to that of a $LiCoO_2$ group cell due to the structure of the $LiMn_2O_4$ itself that remains unstable during the time of charge and discharge.

[0009]

[Problems to be solved by the invention]

In an attempt to eliminate the above-mentioned problems, studies have been conducted on the use of a layered lithium manganese oxide such as $LiMnO_2$ used as a positive electrode material having a different structure from that of the $LiMn_2O_4$. However, when a detailed study of the above-mentioned oxide was done by the inventors, it was discovered that physical properties such as structure and characteristics vary significantly based on the composition of the compounds, in particular, the presence/absence of the elements that comprise the oxide other than Li and Mn, or the types and quantity ratio as well as the process used for forming of the aforementioned oxide.

[0010]

For example, when a fluctuation occurs in the composition of spinel-type lithium manganese oxide ($LiMn_2O_4$) and causes the mean number of Mn to approach 3, the trivalent form, distortion occurs in the crystal structure of above-mentioned oxide to show a phase change from a spinel structure of a cubic system to a tetragonal system and forms $LiMnO_2$. The above-mentioned phase change from cubic system to tetragonal system occurs along with charge and discharge at a potential range near 3V against lithium; thus, it cannot be used in the same manner as the above-mentioned lithium secondary cell in which charge and discharge are done at a voltage close to 4V.

[0011]

Furthermore, when the structural molar ratio of Li and Mn (Li/Mn) is set as 1, crystal structure of $LiCoO_2$ exhibits an orthorhombic system due to the Jahn-Teller effect caused by trivalent Mn.

[0012]

Electrochemical charge and discharge are possible for the above-mentioned compound at an Li quantity ratio in the range of 0 to 1.0, and theoretical discharge capacity is approximately 285 mAh/g. However, with an increase in the ratio of tetravalent Mn during the course of initial

charging, phase transition to a spinel structure occurs, thus, it not only shows a difference in shape of the charge and discharge curve for initial state and charge and discharge curve for the second time and thereafter, but also, discharge capacity shows a considerable reduction from that of the theoretical value when discharging is stopped at 3.5V or higher. Furthermore, the change in structure initiated due to charge and discharge is accompanied by a shift in Mn; thus, cycle durability is insufficient, and quick charge and discharge is not possible.

[0013]

Therefore, in order to put a layered lithium manganese oxide such as $LiCoO_2$ to a practical use, it is necessary to solve problems such as stabilization of the crystal structure, higher capacity through improved reversibility during the course of charge and discharge, and durability during the course of charge and discharge cycle.

[0014]

[Means to solve the problem]

The present invention was achieved as a result of much research conducted in an effort to eliminate the above-mentioned problems, and the purpose of the present invention is to produce a lithium-containing composite oxide having a stable structure, high durability against charge and discharge reversibility and charge and discharge cycle, and high energy density per unit area and to produce a non-aqueous secondary cell that utilizes the above-mentioned material as a positive electrode.

[0015]

The present invention is to produce a lithium-containing composite oxide having the composition indicated by general formula

$Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$

[Wherein, $0 \leq x \leq 0.05$, $-0.05 \leq x+\alpha \leq 0.05$, and $0 \leq y \leq 0.4$, and $-0.1 \leq \delta \leq 0.1$ (provided that $0 \leq y \leq 0.2$) or $-0.24 \leq \delta \leq 0.24$ (provided that $0.2 < y \leq 0.4$), and M is one or more types of elements selected from a

group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn] produced by baking a composite compound containing at least Ni and Mn as structural elements and an Li compound.

[0016]

Furthermore, the present invention is to produce a lithium-containing composite oxide having a composition indicated by the above-mentioned general formula and having diffraction peaks with an angle of diffraction 2θ at or around 18° and around 44° by X-ray diffraction measurement that utilizes CuKα ray, and having two diffraction peaks at 63° to 66°, and furthermore, the ratio of the integrated intensity of the aforementioned diffraction peaks at around 18° I_{18}, and the integrated intensity of the diffraction peak at around 44° I_{44}, I_{44}/I_{18}, and difference of the diffraction angle 2θ of the two diffraction peaks existing at 63° to 66°, θa, are either $0.9<I_{44}/I_{18}\leq1.2$ and $0.3°\leq\theta a\leq0.6°$ (provided that $0\leq y\leq0.2$) or $0.7\leq I_{44}/I_{18}\leq1$ and $0.55°\leq\theta a\leq0.75°$ (provided that $0.2<y\leq0.4$), respectively.

[0017]

Furthermore, the present invention is to produce a lithium-containing composite oxide having a true density in the range of 4.55 to 4.95 g/cm^3.

[0018]

And furthermore, the present invention is to produce a non-aqueous secondary cell with excellent properties such as cycle durability achieved by using a positive electrode in which the above-mentioned non-aqueous secondary cell is used as an active material, a negative electrode, and a non-aqueous electrolyte in combination.

[0019]

[Embodiment of the invention]

The present invention is explained further in specific terms with a suitable embodiment of the present invention. The lithium-containing composite oxide of the present invention is indicated by the following general formula $Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$ [Wherein,

$0 \leq x \leq 0.05$, $-0.05 \leq x+\alpha \leq 0.05$, and $0 \leq y \leq 0.4$, and $-0.1 \leq \delta \leq 0.1$ (provided that $0 \leq y \leq 0.2$) or $-0.24 \leq \delta \leq 0.24$ (provided that $0.2 < y \leq 0.4$), and M is one or more types of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn], and is a composite oxide with a very limited range of composition that includes at least Ni and Mn as structural elements and the quantity ratio of Ni and Mn is 1:1.

[0020]

Reasons for selection of the above-mentioned very limited composition alone as the lithium-containing composite oxide in the present invention are explained below. In other words, as described above, when lithium manganese oxide is used, distortion of the crystal structure occurs due to the Jahn-Teller effect when the ratio of trivalent Mn is increased and reduction in the potential at the time of charge and discharge occurs. Therefore, it is necessary to set the valence of Mn close to tetravalent, and to achieve stabilization of the crystal structure.

[0021]

In relation to the above-mentioned subjects, the inventors considered that it is effective to either increase the mean number of Mn by including excess Li in $LiCoO_2$ or to substitute Mn of $LiCoO_2$ with other elements, for example, Co or Ni, capable of stably forming a layer structure lithium-containing composite oxide, and detailed studies were conducted on the quantity ratio of Li, types of substitution elements, and their quantity ratio.

[0022]

As a result, it was discovered that it was possible to obtain a lithium-containing composite oxide that exhibits a stabilized crystal layer-form structure having reversibility of charge and discharge at a potential in a range close to 4V, and having excellent durability of the charge and discharge cycle by having a composition range as shown below. A composition that is indicated by the general formula of $LiNi_{1/2}Mn_{1/2}O_2$ in which the quantity ratio of Ni and Mn is 1/2:1/2, that is, 1:1, is used as a base, and refers to the composition in which Ni and Mn are each

substituted with Li by x/2 respectively, and quantity ratio of Ni and Mn each slides from 1/2:1/2 by $\delta/2$ and $-\delta/2$ respectively, and the quantity ratio of Li has a width of α, and in addition, Ni and Mn are each substituted with element M (Wherein, M is one or more types of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn) by y/2 respectively, in other words, the composition range shown with a general formula of $Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$ [Wherein, $0 \leq x \leq 0.05$, $-0.05 \leq x+\alpha \leq 0.05$, and $0 \leq y \leq 0.4$, and $-0.1 \leq \delta \leq 0.1$ (provided that $0 \leq y \leq 0.2$) or $-0.24 \leq \delta \leq 0.24$ (provided that $0.2 < y \leq 0.4$), and M is one or more types of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn].

[0023]

It is hypothesized that this is due to that mean valence number of Mn in the lithium-containing composite oxide takes a value that is close to tetravalent (approximately 3.3 to 4), and during doping and undoping of Li upon charge and discharge, the shift of Mn in the crystal is controlled. It should be noted that in the present invention, the value measured by X-ray absorption spectral analysis (XAS) was used as the valence number of Mn.

[0024]

Furthermore, as described above, when X-ray diffraction measurement is done for the lithium-containing composite oxide having at least Ni and Mn as structural elements and shows a stable layer-form structure, charge and discharge reversibility, and excellent durability of the charge and discharge cycle using $CuK\alpha$ rays, it was discovered that a composite oxide of which diffraction pattern shows the same characteristics as those of $LiNiO_2$ indicating presence of one diffraction peak that is the equivalent to the diffraction peaks (003) and (104) of $LiNiO_2$ and are located at and around 18° and 44° diffraction angles 2θ, and at the same time, one each diffraction peak that is equivalent to the diffraction peaks (108) and (110) are located in the range of 63° to 66°, and the diffraction pattern that is the same as that of $LiNiO_2$ was observed.

[0025]

Furthermore, as a result of further studies on the diffraction pattern performed in detail, it was discovered that the material was a single-phase composite oxide having the ratio of the integrated intensity of the aforementioned diffraction peaks at around 18° I_{18}, and the integrated intensity of the diffraction peak at around 44° I_{44}, I_{44}/I_{18}, and difference of the diffraction angle 2θ of the two diffraction peaks exist at 63° to 66°, θa, are either $0.9<I_{44}/I_{18}\leq 1.2$ and $0.3°\leq\theta a\leq 0.6°$ (provided that $0\leq y\leq 0.2$) or $0.7\leq I_{44}/I_{18}\leq 1$ and $0.55°\leq\theta a\leq 0.75°$ (provided that $0.2<y\leq 0.4$), respectively.

[0026]

The charge and discharge curves of the above-mentioned lithium-containing composite oxide exhibit a possible charge and discharge at a voltage range of nearly 4V similar to that of $LiMn_2O_2$ having a spinel-type structure, and the composite oxide can be used as a substitute for $LiCoO_2$ used as a conventional positive electrode active material.

[0027]

Furthermore, the lithium-containing composite oxide having the above-mentioned composition exhibits a true density as high as 4.55 to 4.95 g/cm^3, which indicates the material is capable of forming a high volume energy density. The true density of lithium-containing composite oxide containing a specific range of Mn vary significantly depending on the composition, but the structure is stabilized and single-phase is likely to be produced within the above-mentioned narrow composition range; thus, it is considered to show a large value close to the true density of $LiCoO_2$. In particular, it was discovered that the value becomes high when the composition was close to the stoichiometric ratio, and it was also discovered that the composite oxide having a high density of at least 4.7 g/cm^3 was formed at $-0.015\leq x+\alpha\leq 0.015$.

[0028]

Furthermore, as described above, the lithium-containing composite oxide of the present

invention takes a basic structure where Ni and Mn form 1:1 as in the case of $LiNi_{1/2}Mn_{1/2}O_2$, and further research on the composition showed production of a lithium-containing composite oxide with excellent characteristics is possible when a composition where the quantity ratio of Ni, Mn and M is 1:1:1, that is, at a composition near that indicated by the general formula $LiNi_{1/3}Mn_{1/3}M_{1/3}O_2$.

[0029]

In the above-mentioned general formula $Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$ (Wherein, M is one or more types of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn), only a small value of slippage on the quantity ratio ($\delta/2$) of Ni and Mn within a composition range of $0<y\leq 0.2$ is allowed, but the stability of crystal structure is increased at the composition range of $0.2<y\leq 0.4$ to allow easy formation of a single phase, and as a result, it is possible to obtain the target lithium-containing composite oxide even when the aforementioned slippage of quantity ratio of Ni and Mn may be high. As a result, when it is $0\leq y\leq 0.2$ in the above-mentioned general formula, the range that can be taken by δ becomes as narrow as $-0.1\leq\delta\leq 0.2$, on the other hand, when $0.2<y\leq 0.4$, the range that can be taken by δ becomes as broad as $-0.24\leq\delta\leq 0.24$.

[0030]

Furthermore, it was found that production of a lithium-containing composite oxide having I_{44}/I_{18} in the range of 0.7 to 1 and at the same time, θa in the range of 0.55° to 0.75° when measurements were made of the X-ray diffraction using $CuK\alpha$ ray at the composition range $0.2<y\leq 0.4$. It was further found that the true density becomes higher than the composition range of $0\leq y\leq 0.2$ (approximately 4.75 to 4.95 g/cm^3 in stoichiometric composition) and a material with a higher volume energy density could be produced.

[0031]

In this case, in a composition of y>4, in other words, when the substitution rate of

element M becomes 0.4 or higher, a hetero phase is formed in the target composite oxide, and stability of the compound is likely to be lost; thus, the substitution rate y for element M is limited to 0.4 or below.

[0032]

Furthermore, it is disclosed in publications such as Japanese Patent No. 3064655, Japanese Patent No. 3130813, Japanese Kokai [Unexamined] Patent Application No. Hei 9-199127, and Japanese Kokai [Unexamined] Patent Application No. 2000-294242 that production of a positive electrode positive material for non-aqueous secondary cells could be made possible in a very wide composition range that includes the composition range of the lithium-containing composite oxide of the present invention. However, none of the above-mentioned prior art discloses the possible production of a lithium-containing composite oxide having exceptionally excellent characteristics at a composition range limited to nearby 1:1 Ni and Mn in the present invention, and furthermore, the present invention cannot be easily conceived from the above-mentioned prior art.

[0033]

Incidentally, it is very difficult to form a single phase in the above-mentioned lithium-containing composite oxide by simply mixing Li compound and Mn compound and Ni compound, etc. together and baking the mixture.

[0034]

It is hypothesized that uniform diffusion is made difficult in the synthesis reaction due to the slow diffusion rate in solids such as Ni and Mn, thus, uniform distribution of the aforementioned elements in the oxide produced is not possible.

[0035]

As a result of performing further detailed studies on the method for synthesizing the above-mentioned oxide, the present inventors discovered that a single phase of the lithium-

containing composite oxide of the present invention can be synthesized with relative ease by baking a composite compound containing at least Ni and Mn as structural elements and a Li compound. In other words, forming of a single phase can be easily accomplished when a composite compound containing Ni and Mn as the structural elements is synthesized ahead of time, and baking the above-mentioned composite compound along with a Li compound so as to uniformly distribute the aforementioned metal elements during the course of oxide forming reaction. Needless to say, the synthesis method of the lithium-containing composite oxide of the present invention is not limited to the above-mentioned method, and it seems that the physical properties of the composite oxide produced as described above, namely, stability of structure, reversibility of charge and discharge, true density and the like, etc. change significantly depending on the type of synthesis process used.

[0036]

In this case, as the aforementioned composite compound that includes at least Ni and Mn as structural elements, for example, co-precipitated compounds containing at least Ni and Mn, compounds prepared through a hydrothermal synthesis, or compounds prepared through a mechanical synthesis, and compounds prepared through heat-treatment on these may be used. And oxides of Ni and Mn or hydroxides such as $Ni_{0.5}Mn_{0.5}(OH)_2$, $NiMn_2O_4$, or $Ni_{0.5}Mn_{0.5}OOH$, etc. may be used effectively. Furthermore, in synthesis of a lithium-containing composite oxide that includes M (Wherein, M is one or more types of elements selected from the group of Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn) as structural elements, the aforementioned oxide can be produced by mixing a composite compound containing at least Ni and Mn, Li compound, and compound that includes M and baking is performed, and it is desirable to use the composite compound containing Ni, Mn, and M to start with, when possible. And furthermore, the quantity ratio of Ni, Mn, and M in the above-mentioned composite oxide can be selected appropriately in accordance with the composition of the target lithium-containing composite oxide.

[0037]

Furthermore, for the Li compound, a variety of lithium salts may be used, and for example, lithium hydroxide-monohydrate, lithium nitrate, lithium carbonate, lithium acetate, lithium bromide, lithium chloride, lithium citrate, lithium fluoride, lithium iodide, lithium lactate, lithium oxalate, lithium phosphate, lithium pyruvate, lithium sulfate, lithium oxide, etc. can be mentioned, and among those listed above, lithium hydroxide-monohydrate is further desirable from the standpoint of not generating carbon dioxide gas, nitrogen oxide gas, sulfur oxide gas, etc. that has an adverse effect on the environment.

[0038]

Mixing of the above-mentioned composite compound containing at least Ni and Mn as structural elements and a Li compound is done nearly in accordance with the ratio of the composition of the target lithium-containing composite oxide, and for example, synthesis of the lithium-containing composite oxide of the present invention can be carried out when baking is done for the aforementioned mixture in an atmosphere containing oxygen at a temperature of 700 to 1100°C for 1 to 24 hours.

[0039]

As for the heat-treatment used for the above-mentioned baking, rather than increasing the temperature to the specific temperature all at once, it is desirable when heating is done at a temperature below the baking temperature (approximately 250 to 850°C) ahead of time, and a preheat-treatment is performed, then, the temperature is increased to the baking temperature to promote the reaction. The reason is because the reaction between the Li compound and the composite compound containing at least Ni and Mn as structural elements appears to occur in a stepwise fashion and the final product lithium-containing composite oxide is appears to be produced via an intermediate product. In other words, when the temperature is increased to the baking temperature all at once, a part of the reaction between the Li compound and the composite

compound containing at least Ni and Mn as structural elements reaches the final stage reaction, and thus, reaction of a non-reacting material is blocked by the lithium-containing composite oxide generated or uniformity of the composition is lost. And furthermore, stepwise heat-treatment is effective for reduction of the time required for the reaction process and to produce a uniform composite compound, as well. The above-mentioned pre-heating time is not especially limited, and in general, 0.5 to 30 hours is used.

[0040]

Furthermore, in the process where baking is performed for the mixture of the aforementioned lithium compound and composite compound containing at least Ni and Mn as structural elements, the dry mixture may be used as is, but when the mixture is first dispersed in a solvent such as ethanol to form a slurry, mixing is done by a planetary ball mill, etc. for 30 to 60 minutes, and when the mixture is dried and used, uniformity of the compound synthesized can be further increased.

[0041]

For the atmosphere used for the above-mentioned heat-treatment, an atmosphere containing oxygen, that is in air, mixed atmosphere consisting of an inert gas such as argon, helium, and nitrogen, and oxygen or oxygen can be used. It is desirable when the ratio of oxygen in the atmosphere is in the range of 10% to 100% in terms of the volume ratio.

[0042]

The flow ratio of the above-mentioned gas is preferably at least 1 dm^3/min per 100 g of the aforementioned mixture, and in the range of 1 to 5 dm^3/min is further desirable. When the gas flow ratio is low, that is, when the gas flow velocity is slow, the reaction progresses heterogeneously and impurities such as Mn_2O_3 and Li_2MnO_3 are likely to be generated.

[0043]

When the lithium-containing composite oxide of the present invention produced as

described above is used as a positive electrode active material, production of a non-aqueous secondary cell can be achieved according to the method described below.

[0044]

Production of a positive electrode is carried out as mixing is done for the above-mentioned lithium-containing composite oxide with an optional electrically conductive coagent such as acetylene black and a binder such as polytetrafluoroethylene and polyvinylidene fluoride and the positive electrode agent produced can be used as is or further coated onto or impregnated into a substrate that functions as a current collector and solidified with the substrate and used. For the substrate used in this case, for example, a mesh of metals such as aluminum, stainless steel, titanium, or copper, and furthermore, punched metal, expanded metal, metal form, metal foil, etc. can be used.

[0045]

Furthermore, for the negative electrode active material used in correspondence with the above-mentioned positive electrode, in general, lithium or lithium-containing compound is used, and for examples of lithium-containing compounds, lithium alloys such as Li-Al alloy, Li-Pb alloy, Li-In alloy, and Li-Ga alloy, elements that can be formed into alloys with lithium such as Si, Sn, and Mg-Si alloy, or alloys of the aforementioned elements can be mentioned. Furthermore, in addition to oxide type materials such as Sn oxide and Si oxide, carboneous materials such as graphite and fibrous fiber, lithium-containing composite nitride, etc. may be used. Furthermore, composites of the above-mentioned materials may be used as active materials as well. Production of the negative electrode can be carried out according to the production method of the above-mentioned positive electrode as well.

[0046]

The quantity ratio of the active material in the above-mentioned positive electrode and negative electrode varies depending on the type of negative electrode active material used as

well, and in general, characteristics of the positive electrode can be utilized effectively when the positive electrode active material/negative electrode active material=1.5 to 3.5 (volume ratio).

[0047]

For the non-aqueous electrolyte used in the lithium-containing composite oxide of the present invention, a liquid electrolyte of an organic solvent type produced by dissolving an electrolyte in an organic solvent, that is, for the electrolyte, a polymer electrolyte in which the aforementioned electrolyte is retained in a polymer, etc. can be used. The organic solvent included in the electrolyte or polymer is not especially limited, and from the standpoint of negative characteristics, it is desirable when a chain ester is included. For the above-mentioned chain ester, chain carbonates represented with dimethyl carbonate, diethyl carbonate, and ethylmethyl carbonate, and organic solvents such as ethyl acetate and methyl propionate can be mentioned. Furthermore, one type may be used, or two or more different types of the above-mentioned chain esters may be mixed and used in combination, and for improvement in the low-temperature characteristics, it is desirable when at least 50 vol% of the above-mentioned chain ester is included in the entire organic solvent, and it is further desirable when at least 65 vol% of the above-mentioned chain ester is included for the total organic solvent.

[0048]

In this case, it is desirable when an ester having high dielectric constant (dielectric constant: at least 30) is mixed with the above-mentioned chain ester for an increase in discharge capacity rather than for the organic solvent to be comprised of the above-mentioned chain ester alone. For specific examples of the above-mentioned esters, cyclic carbonates represented by ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate, γ-butyrolactone, ethylene glycol sulfite, etc. can be mentioned, and in particular, cyclic structured esters such as ethylene carbonate and propylene carbonate are further desirable.

[0049]

From the standpoint of discharge capacity, it is desirable when at least 10 vol%, preferably, at least 20 vol%, of the above-mentioned ester with a high dielectric constant is included for the total amount of organic solvent. On the other hand, from the standpoint of negative characteristics, not more than 40 vol% is desirable, and not more than 30 vol% is further desirable.

[0050]

Furthermore, for the solvent used in combination with the above-mentioned ester with a high dielectric constant, for example, 1,2-dimethoxy ethane, 1,3-dioxolane, tetrahydrofuran, 2-methyl- tetrahydrofuran, diethyl ether, etc. can be mentioned. In addition, amine imide type organic solvents, sulfur-containing or nitrogen-containing organic solvents, etc. may be used as well.

[0051]

For the electrolyte dissolved in the organic solvent, for example, $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiSbF_6$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiCF_3CO_2$, $Li_2C_2F_4(SO_3)_2$, $LiN(CF_3SO_2)_2$, $LiC(CF_3SO_2)_3$, $LiC_nF_{2n+1}SO_3$ ($n \geq 2$) may be used independently or in combination. In particular, $LiPF_6$ and $LiC_4F_9SO_3$ capable of achieving excellent charge and discharge characteristics are further desirable. Furthermore, the concentration of the electrolyte in the electrobath is not especially limited and approximately 0.3 to 1.7 mol/dm^3 is desirable, and 0.4 to 1.5 mol/dm^3 is further desirable.

[0052]

Furthermore, in order to improve safety and storage stability of the cell, aromatic compounds may be included in the non-aqueous electrolyte. For examples of aromatic compounds, benzenes having an alkyl group such as cyclohexylbenzene and t-butyl benzene, biphenyl, fluorobenzenes, etc. can be used effectively.

[0053]

For the separator, those having an adequate strength and capable of retaining a high proportion of the electrolyte are desirable, for example, microporous films and non-woven fabrics made of polypropylene, polyethylene, copolymer of propylene and ethylene, etc. having a thickness in the range of 5 to 50 μm can be used effectively. When a thin separator with a thickness of 5 to 20 μm is used, cell characteristics such as charge and discharge cycle and high temperature storage are likely to deteriorate, but the lithium-containing composite oxide of the present invention has high stability; thus, function of the cell can be stably achieved even when the above-mentioned thin separator is used.

[0054]

[Working Examples]

The present invention is explained in further detail with working examples below. It should be noted that the present invention is not limited to the working examples shown.

[0055]

(Working Example 1)

Sodium hydroxide was added to a 2 vol% of aqueous ammonia to form a pH of approximately 12; then, a mixed solution containing 1 mol/dm^3 each of nickel sulfate and manganese nitrate was added dropwise at a rate of 46 ml/min and 25 vol% of aqueous ammonia was added dropwise at a rate of 3.3 ml/min each from a quantitative pump as stirring was being performed, and formation of a coprecipitate compound of Ni and Mn was formed. In this case, the temperature of the reaction solution was retained at 50°C, and sodium hydroxide solution with a concentration of 3.2 mol/dm^3 was added dropwise so as to maintain the pH of the reaction solution at around 12. Furthermore, purging with nitrogen gas was performed at a ratio of 1 dm^3/min to maintain an inert atmosphere for the reaction solution.

[0056]

The reaction product produced was subjected to a water wash, filtration, and drying to

form an hydroxide containing Ni and Mn at a ratio of 1:1, and measurement was performed for 0.2 mol of the above-mentioned hydroxide and 0.198 mol of $LiOH{\cdot}H_2O$ to form a mixture; then, dispersing of the above-mentioned mixture was done in ethanol to form a slurry; furthermore, mixing was performed for 40 min by a planetary ball mill, and drying was done at room temperature. Furthermore, the above-mentioned mixture was placed in an aluminum crucible, heating to a temperature of 800°C was done in an air current of 1 dm^3/min, and the above-mentioned temperature was retained for 2 hours and a pre-heat treatment was achieved. Subsequently, the temperature was increased to 1000°C and baking was performed for 12 hours and synthesis of a lithium-containing composite oxide was achieved. The oxide produced in this manner was crushed in a mortar to form a powder and stored in a desiccator.

[0057]

When measurements were made of the above-mentioned powder of the oxide by an atomic absorption spectrophotometer, the powder had a composition of $Li_{0.99}Ni_{0.5}Mn_{0.5}O_2$. Furthermore, for measurement of the analysis of the state of the above-mentioned compound, X-ray absorption spectral analysis was performed for Mn by a BL4 beam port of super-conductive small radiation source (product of Sumitomo Denko Co., Aurora) of SR Center of the University of Ritsumeikan. The analysis of the data obtained was done according to the reference [Journal of the Electrochemical Society, 146 p2799-2809 (1999)] by analysis software REX (product of Rigaku Denki Co.). Furthermore, in order to determine the value number of Mn in the above-mentioned compound, MnO_2 and $LiNi_{0.5}Mn_{1.5}O_4$ (both are reference samples of compounds having Mn of mean value number of 4) $LiMn_2O_4$ (reference sample of compound having Mn of mean value number of 3.5), $LiMn_2O_4$ and Mn_2O_3 (both are reference samples of compound having Mn of mean value number of 3) and MnO (reference sample of compound having Mn of mean value number of 2). The regression line that shows the relationship between the K absorption end position of the Mn and value number of Mn of each reference sample was

obtained, and as a result, the K absorption end position of Mn of the above-mentioned compound was same as the K absorption end position of MnO_2 and $LiNi_{0.5}Mn_{1.5}O_4$; thus, the mean value number of the Mn of the above-mentioned compound was determined as approximately 4.

[0058]

A compound suitable for a reference sample having Ni value number of 3 or higher was not available for Ni, as a consequence, it was not possible to obtained an accurate value number, but the K absorption end position of NiO, which is a compound having Ni of mean value number 2 and the K absorption end position of $LiNi_{0.5}Mn_{1.5}O_4$ were the same; thus, the mean value number of Ni of the above-mentioned compound was estimated to be approximately 2.

[0059]

(Working Example 2)

Measurement was done for 0.198 mol of hydroxide containing Ni and Mn at a ratio of 1:1 synthesized as in the case of Working Example 1 and 0.202 mol of $LiOH{\cdot}H_2O$, and synthesis of a lithium-containing composite oxide indicated by $Li_{1.01}Ni_{0.495}Mn_{0.495}O_2$ was carried out as described above.

[0060]

(Working Example 3)

Measurement was done for 0.196 mol of hydroxide containing Ni and Mn at a ratio of 1:1 synthesized as in the case of Working Example 1 and 0.204 mol of $LiOH{\cdot}H_2O$, and synthesis of a lithium-containing composite oxide indicated by $Li_{1.02}Ni_{0.49}Mn_{0.49}O_2$ was carried out as described above.

[0061]

(Working Example 4)

Measurement was done for 0.194 mol of hydroxide containing Ni and Mn at a ratio of 1:1

synthesized as in the case of Working Example 1 and 0.206 mol of $LiOH \cdot H_2O$, and synthesis of a lithium-containing composite oxide indicated by $Li_{1.03}Ni_{0.485}Mn_{0.485}O_2$ was carried out as described above.

[0061]

(Working Example 5)

Measurement was done for 0.192 mol of hydroxide containing Ni and Mn at a ratio of 1:1 synthesized as in the case of Working Example 1 and 0.208 mol of $LiOH \cdot H_2O$, and synthesis of a lithium-containing composite oxide indicated by $Li_{1.04}Ni_{0.48}Mn_{0.48}O_2$ was carried out as described above.

[0063]

(Working Example 6)

Measurement was done for 0.19 mol of hydroxide containing Ni and Mn at a ratio of 1:1 synthesized as in the case of Working Example 1 and 0.21 mol of $LiOH \cdot H_2O$, and synthesis of a lithium-containing composite oxide indicated by $Li_{1.05}Ni_{0.475}Mn_{0.475}O_2$ was carried out as described above.

[0064]

(Working Example 7)

A mixed solution containing 0.9 mol/dm^3 of nickel sulfate, 0.9 mol/dm^3 of manganese nitrate and 0.2 mol/dm^3 cobalt sulfate was added dropwise and production of a hydroxide containing Ni, Mn, and Co at a ratio of 4.5:4.5:1 was produced as in the case of Working Example 1. Furthermore, synthesis of a lithium-containing composite oxide indicated by $Li_{0.99}Ni_{0.45}Mn_{0.45}CO_{0.1}O_2$ was carried out as in the case of Working Example 1.

[0065]

(Working Example 8)

A mixed solution containing 0.75 mol/dm^3 of nickel sulfate, 0.75 mol/dm^3 of manganese

nitrate and 0.5 mol/dm^3 cobalt sulfate was added dropwise and synthesis of a lithium-containing composite oxide indicated by $Li_{0.99}Ni_{0.375}Mn_{0.375}CO_{0.25}O_2$ was carried out as in the case of Working Example 1.

[0066]

(Working Example 9)

A mixed solution containing 0.67 mol/dm^3 of nickel sulfate, 0.66 mol/dm^3 of manganese nitrate and 0.66 mol/dm^3 cobalt sulfate was added dropwise and synthesis of a lithium-containing composite oxide indicated by $Li_{0.99}Ni_{0.34}Mn_{0.33}CO_{0.33}O_2$ was carried out as in the case of Working Example 1.

[0067]

(Working Example 10)

A mixed solution containing 0.6 mol/dm^3 of nickel sulfate, 0.6 mol/dm^3 of manganese nitrate and 0.8 mol/dm^3 cobalt sulfate was added dropwise and synthesis of a lithium-containing composite oxide indicated by $Li_{0.99}Ni_{0.3}Mn_{0.3}CO_{0.4}O_2$ was carried out as in the case of Working Example 1.

[0068]

(Comparative Example 1)

Measurement was performed for 0.2 mol of $LiOH \cdot H_2O$ and 0.2 mol of MnOOH, and mixing was carried out for 30 min by a planetary ball mill, the above-mentioned mixture was placed in an aluminum crucible, and baked at a temperature of 450°C in nitrogen stream of 1 dm^3/min for 10 hours and synthesis of a orthorhombic system lithium manganese oxide indicated by $LiMnO_2$ was achieved.

[0069]

(Comparative Example 2)

Measurement was performed for 0.18 mol of a hydroxide containing Ni and Mn at a ratio

of 1:1 synthesized as in the case of Working Example 1 and 0.22 mol of $LiOH \cdot H_2O$ and synthesis of the lithium-containing composite oxide indicated by $Li_{1.1}Ni_{0.45}Mn_{0.45}O_2$ was carried out as in Working Example 1.

[0070]

(Comparative Example 3)

A mixed solution containing 0.5 mol/dm^3 of nickel sulfate, 0.5 mol/dm^3 of manganese nitrate and 1 mol/dm^3 cobalt sulfate was added dropwise and synthesis of a lithium-containing composite oxide indicated by $Li_{0.99}Ni_{0.25}Mn_{0.25}Co_{0.5}O_2$ was carried out as in Working Example 1.

[0071]

(Comparative Example 4)

A mixed solution containing 0.4 mol/dm^3 of nickel sulfate, 0.4 mol/dm^3 of manganese nitrate and 1.2 mol/dm^3 cobalt sulfate was added dropwise and synthesis of a lithium-containing composite oxide indicated by $Li_{0.99}Ni_{0.2}Mn_{0.2}Co_{0.6}O_2$ was carried out as in Working Example 1.

[0072]

(Comparative Example 5)

A mixed solution containing 0.6 mol/dm^3 of nickel sulfate and 1.5 mol/dm^3 of manganese nitrate was added dropwise and synthesis of a lithium-containing composite oxide indicated by $Li_{0.99}Ni_{0.25}Mn_{0.25}O_2$ was carried out as in Working Example 1.

[0073]

(Comparative Example 6)

In Working Example 7, 1.2 mol/dm^3 of nickel sulfate and 1.2 mol/dm^3 of manganese nitrate were used and synthesis of a lithium-containing composite oxide indicated by $Li_{0.99}Ni_{0.6}Mn_{0.3}Co_{0.1}O_2$ was carried out. In this case, the quantity ratio of Ni and Mn alone in the lithium-containing composite oxide of Comparative Example 6 is different from those of Ni and Mn of Working Example 7.

[0074]

(Reference example)

Measurement was performed for 0.2 mol of $LiOH{\cdot}H_2O$, 0.1 mol of $Ni(OH)_2$ and 0.1 mol of MnOOH, and mixing was performed for 30 min by a planetary ball mill to form a mixture, and the above-mentioned mixture was placed in an aluminum crucible, and baking was done at a temperature of 800°C in air for 10 hours and synthesis of a lithium-containing composite oxide indicated by $LiNi_{0.5}Mn_{0.5}O_2$ was carried out.

[0075]

List of lithium-containing composite oxides synthesized in the above-mentioned Working Examples 1 to 10, Comparative Examples 1 to 6 and reference example are shown in Table I below.

[0076]

[Table I]

	Composition [$Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$]				
		x	x+α	y	δ
Work Ex. 1	$Li_{0.99}Ni_{0.5}Mn_{0.5}O_2$	0	-0.01	0	0
Work Ex. 2	$Li_{1.01}Ni_{0.495}Mn_{0.495}O_2$	0.01	0.01	0	0
Work Ex. 3	$Li_{1.02}Ni_{0.49}Mn_{0.49}O_2$	0.02	0.02	0	0
Work Ex. 4	$Li_{1.03}Ni_{0.485}Mn_{0.485}O_2$	0.03	0.03	0	0
Work Ex. 5	$Li_{1.04}Ni_{0.48}Mn_{0.48}O_2$	0.04	0.04	0	0
Work Ex. 6	$Li_{1.05}Ni_{0.475}Mn_{0.475}O_2$	0.05	0.05	0	0
Work Ex. 7	$Li_{0.99}Ni_{0.45}Mn_{0.45}Co_{0.1}O_2$	0	-0.01	0.1	0
Work Ex. 8	$Li_{0.99}Ni_{0.375}Mn_{0.375}Co_{0.25}O_2$	0	-0.01	0.25	0
Work Ex. 9	$Li_{0.99}Ni_{0.34}Mn_{0.33}CO_{0.33}O_2$	0	-0.01	0.33	0.01
Work Ex. 10	$Li_{0.99}Ni_{0.3}Mn_{0.3}Co_{0.4}O_2$	0	-0.01	0.4	0
Comp Ex. 1	$LiMnO_2$	0	0	0	-1
Comp Ex. 2	$Li_{1.1}Ni_{0.45}Mn_{0.45}O_2$	0.1	0.1	0	0
Comp Ex. 3	$Li_{0.99}Ni_{0.25}Mn_{0.25}Co_{0.5}O_2$	0	-0.01	0.5	0
Comp Ex. 4	$Li_{0.99}Ni_{0.2}Mn_{0.2}Co_{0.6}O_2$	0	-0.01	0.6	0
Comp Ex. 5	$Li_{0.99}Ni_{0.25}Mn_{0.75}O_2$	0	-0.01	0	-0.5
Comp Ex. 6	$Li_{0.99}Ni_{0.6}Mn_{0.3}Co_{0.1}O_2$	0	-0.01	0.1	0.3
Ref. Ex.	$LiNi_{0.5}Mn_{0.5}O_2$	0	0	0	0

[0077]

An X-ray diffraction test was performed for lithium-containing composite oxides produced in the above-mentioned Working Examples of the present invention, Comparative Examples, and Reference Example using CuKα ray. The lithium-containing composite oxides produced in Working Examples of the present invention, Comparative Examples 2 to 6 and Reference Example showed an X-ray diffraction pattern almost identical to those of $LiNiO_2$ having a layer structure, but peaks that indicate formation of a different phase were observed in the X-ray diffraction pattern of Comparative Examples 3 to 5 and the Reference Example, as well. Furthermore, the X-ray diffraction pattern showed a orthorhombic system pattern different from that of $LiNO_2$. The peak based on formation of different phase was not observed in Working Examples of the present invention, Comparative Example 2 and Comparative Example 6, in other words, each diffraction peak was observed at 18° and at 44° of diffraction angle of 2θ, and two diffraction peaks are observed at 63° to 66°, thus, it was confirmed that the oxide produced was a single phase lithium-containing composite oxide having a structure similar to that of $LiNiO_2$. Furthermore, the peak based on Kα_2 ray adjacent to the peak based on the Kα_1 ray of Cu was observed in a diffraction peak within 63° to 66°, but in the present invention, the aforementioned peak based on Kα_2 ray alone is considered as the diffraction peak existing within 63° to 66°.

[0078]

Among those, X-ray diffraction patterns of Working Example 1, Working Example 8, Working Example 9, Comparative Example 4 and Comparative Example 5 are shown in Fig. 1 to Fig. 5.

[0079]

Furthermore, the ratio of the integrating intensity of the diffraction peak at around 18° I_{18}, and the integrated intensity of the diffraction peak at around 44° I_{44}, I_{44}/I_{18}, and the difference in

the diffraction angle θa of the two diffraction peaks existing at 63° to 66° are shown in Table II below. It should be noted that three diffraction peaks are observed within 63° to 66° due to formation of different phases in the lithium-containing composite oxides of Comparative Examples 3 to 5 and Reference example; thus, the above-mentioned data is not included in Table II.

[0080]

[Table II]

	X-ray diffraction measurement		True density (g/cm^3)
	Integrated intensity ratio I_{44}/I_{18}	Difference in the diffraction angle 2θ (degrees)	
Work Ex 1	1.13	0.313	4.74
Work Ex 2	1.14	0.348	4.72
Work Ex 3	1.10	0.390	4.68
Work Ex 4	1.11	0.435	4.65
Work Ex 5	1.08	0.510	4.62
Work Ex 6	1.06	0.555	4.57
Work Ex 7	1.04	0.553	4.75
Work Ex 8	0.88	0.672	4.76
Work Ex 9	0.83	0.700	4.80
Work Ex 10	0.77	0.617	4.82
Comp Ex 1	--	--	4.20
Comp Ex 2	0.99	0.625	4.38
Comp Ex 3	--	--	4.83
Comp Ex 4	--	--	4.90
Comp Ex 6	0.83	0.600	4.65

[0081]

In the lithium-containing composite oxides of Working Examples 1 to 7 where $0 \leq y \leq 0.2$, the integrated intensity ratio I_{44}/I_{18} is within 0.9 to 1.2, and at the same time, the difference in the diffraction angle θa is within 0.55° to 0.75°. On the other hand, in Comparative Example 2 and Comparative Example 6 where the composition is outside the range of the claims of the present invention, either I_{44}/I_{18} or θa is outside the above-mentioned range, and in Comparative Examples 3 to 5 and the Reference example, three diffraction peaks were observed within 63° to 66°, as described above.

[0082]

Furthermore, measurements were made of the true density of the lithium-containing composite oxides of Working Examples of the present invention, Comparative Examples 1 to 4 and Comparative Example 6 using a true density measurement device. And the results obtained are shown in Table II as well. In this case, the measurement error was maximum of ± 0.03 g/cm^3.

[0083]

The true density of the lithium-containing composite oxides of Working Examples the present invention is high, at least 4.7 g/cm^3, in Working Example 1, Working Example 2 and Working Examples 7 to 10 in which the composition is essentially the stoichiometric composition, that is, $-0.015 \leq x+\alpha \leq 0.015$, and a high value of at least 4.75 g/cm^3 was achieved in Working Examples 8 to 10 where $0.2 < y \leq 0/4$. Furthermore, a relatively high value of the true density in the range of 4.57 to 4.68 g/cm^3 was achieved in Working Examples 3 to 6, where the composition is outside the stoichiometric composition.

[0084]

On the other hand, the true density of a conventional orthorhombic system composite oxide of Comparative Example 1 and Comparative Example 2 where the composition is far from the stoichiometric composition is low 4.5 g/cm^3 or below, and furthermore, the true density is

lower in Comparative Example 6 where the ratio of Ni and Mn is outside the present invention in comparison to those of the above-mentioned Working Example 1, Working Example 2 and Working Examples 7 to 10 of the present invention despite the stoichiometric composition.

[0085]

Furthermore, the true density of the lithium-containing composite oxides of Comparative Example 3 and Comparative Example 4 is higher than those of Working Examples of the present invention, but the apparent value is high due to formation of $LiCoO_2$ phase having a true density of approximately 5.1 g/cm^3, and this does not mean that a composite oxide with the true density shown in Table II was produced as a single phase.

[0086]

Furthermore, measurement was performed for the discharge capacity of the lithium-containing composite oxides produced in Working Examples 1 to 10 of the present invention and Comparative Examples 1 and 2 according to the method described below.

[0087]

For 20 parts by mass of polyvinylidene fluoride used as a binder, 250 parts by mass of N-methyl-2-pyrrolidone was added and heating was performed to 60°C and dissolving of polyvinylidene fluoride was done in N-methyl-2-pyrrolidone and production of a binder solution was carried out. For the binder solution produced, 450 parts by mass of the above-mentioned composite oxide was added as a positive electrode active material, and furthermore, 5 parts by mass of carbon black and 25 parts by mass of graphite were added as electrically conductive coagents and stirring was provided to produce a paint slurry. The above-mentioned paint was uniformly coated on both surfaces of an aluminum foil with a thickness of 20 μm and dried and compression molding was done by a roller press machine, and the coated foil was cut to form a positive electrode strips of 483 mm x 54 mm with a mean thickness of 190 μm.

[0088]

The positive electrode produced as described above, and a negative electrode made of a lithium foil were used, and a separator made of a microporous polyethylene film with a thickness of 25 μm was arranged between each of the above-mentioned electrode, and furthermore, an non-aqueous solution prepared by dissolving 1.0 mol/dm^3 of $LiPF_6$ in a mixed solvent of ethylene carbonate and ethylmethyl carbonate of 1:3 volume ratio was used as an electrolyte, a reference electrode of lithium was arranged and assembly of a cell used for capacity evaluation of positive electrode was achieved.

[0089]

The current density for the area of the positive electrode of 0.2 mA/cm^2 was used, and charging was performed for the above-mentioned cell to 4.3 V, and discharge was performed to 3.1 V at the same current density and the discharge capacity was measured. The measured discharge capacity was converted to a value per unit weight of the positive electrode active material (mAh/g) and per unit volume (mAh/cm^3) and values obtained are shown in Table III below. Furthermore, the discharge curves of the positive electrode of cells made of the lithium-containing composite oxides of Working Example 1, Working Example 6, Working Example 8, Comparative Example 1 and Comparative Example 2 are shown in Fig. 6.

[0090]

[Table III]

	Discharge capacity	
	(mAh/g)	(mAh/cm^3)
Working Example 1	148	702
Working Example 2	145	684
Working Example 3	143	669
Working Example 4	141	656
Working Example 5	139	642
Working Example 6	136	622
Working Example 7	150	713
Working Example 8	152	724
Working Example 9	153	731
Working Example 10	153	737
Comparative Example 1	70	294
Comparative Example 2	112	491

[0091]

Operation is possible for the composite oxides of Working Examples 1 to 10 of the present invention at a high discharge potential of at least 3.5 V, and they exhibited high discharge capacities of 136 to 153 mAh/g, but the discharge capacity of those of the comparative examples was low, 120 mAh/g or below, and furthermore, the true density of the oxides of the present invention is high; thus, the above-mentioned difference was more obvious when converted to the discharge capacity per unit area.

[0092]

Furthermore, in order to evaluate characteristics of the non-aqueous secondary cell, the positive electrode active materials of Working Example 1, Working Example 9, Comparative Example 6 and $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ used in commercial non-aqueous secondary cells were used and production of non-aqueous secondary cells was carried out according to the method described below.

[0093]

For the positive electrode, a paste produced by mixing 92 parts by mass of positive electrode active material, 4.5 parts by mass of synthetic graphite, 0.5 parts by mass of carbon black, and 3 parts by mass of polyvinylidene fluoride was coated onto an Al foil substrate and dried, and compression molding was performed.

[0094]

For the negative electrode, a paste produced by mixing 92 parts by mass of natural graphite, 3 parts by mass of low crystalline carbon, and 53 parts by mass of polyvinylidene fluoride was coated onto a Cu foil substrate and dried, and compression molding was performed.

[0095]

The above-mentioned positive electrode and negative electrode were wrapped around with a separator made of a microporous polyethylene film with a thickness of 16 μm in between, and an electrolyte produced by dissolving $LiPF_6$ in a 1:2 volume ratio mixed solution of ethylene carbonate and ethylmethyl carbonate at a concentration of 1.2 mol/dm^3 was used and production of a cylindrical non-aqueous secondary cell with a capacity of approximately 600 mAh was achieved.

[0096]

An evaluation was made of the cycle characteristic and high temperature storage stability of the above-mentioned non-aqueous secondary cells.

[0097]

Evaluation of the cycle characteristic was done based on the discharge capacity after 100 cycles compared to the discharge capacity of the initial cycle when charging and discharging was done at 1C current [capacity retaining rate (%)].

[0098]

Evaluation of high temperature storage stability was performed based on change in the discharge capacity before and after the storage when a storage test was done where the cell was kept for 20 days at 60°C; in other words, comparison was made for the discharge capacity before and after charge and discharge was performed under 1C current and the capacity after storage was compared with the capacity before storage [capacity retaining rate (%)]. And the results of the above-mentioned evaluations are shown in Table IV below.

[0099]

[Table IV]

Positive electrode active material	Cycle characteristic	High temperature storage characteristic
	Capacity retaining rate (%)	Capacity retaining rate (%)
Working Example 1	96	97
Working Example 9	98	98
Comparative Example 6	92	87
$LiCoO_2$	88	91
$LiNi_{0.8}Co_{0.2}O_2$	93	90

[0100]

Excellent cycle characteristic and high temperature storage stability were observed in non-aqueous secondary cells where the lithium composite oxides of Working Example 1 and Working Example 9 were used despite use of a thin separator with a thickness of 16 μm. On the other hand, cycle characteristics and high temperature storage stability were not adequate in Comparative Example 6 where the composition is outside the range of the present invention, and non-aqueous secondary cells where $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ are used as positive electrode active materials as in commercial non-aqueous secondary cells.

[0101]

[Effect of the invention]

As explained above, according to the present invention, it is possible to produce a lithium-containing composite oxide having a composition indicated by the general formula $Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$ [Wherein, $0 \leq x \leq 0.05$, $-0.05 \leq x+\alpha \leq 0.05$, and $0 \leq y \leq 0.4$, and $-0.1 \leq \delta \leq 0.1$ (provided that $0 \leq y \leq 0.2$) or $-0.24 \leq \delta \leq 0.24$ (provided that $0.2 < y \leq 0.4$), and M is one or more types of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn] with high crystalline structure stability, excellent reversibility of charge and discharge and high density.

[0102]

Furthermore, it is possible to produce a high capacity non-aqueous secondary cell when the above-mentioned composite oxide is used as a positive electrode active material. Furthermore, the above-mentioned composite oxide utilizes naturally available low-cost Mn as one of the main structural elements; thus, it is suitable for mass production and cost reduction is possible.

[Brief description of the figures]

[Fig. 1]

The X-ray diffraction pattern of the lithium-containing composite oxide synthesized in Working Example 1 of the present invention.

[Fig. 2]

The X-ray diffraction pattern of the lithium-containing composite oxide synthesized in Working Example 8 of the present invention.

[Fig. 3]

The X-ray diffraction pattern of the lithium-containing composite oxide synthesized in Working Example 9 of the present invention.

[Fig. 4]

The X-ray diffraction pattern of the lithium-containing composite oxide synthesized in Comparative Example 4 of the present invention.

[Fig. 5]

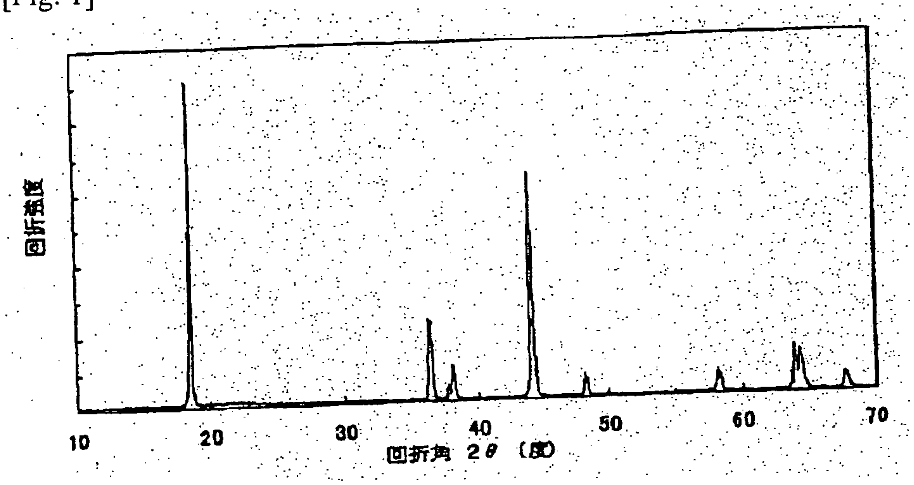
The X-ray diffraction pattern of the lithium-containing composite oxide synthesized in Comparative Example 5 of the present invention.

[Fig. 6]

The discharge curves of the positive electrode of cells made of the lithium-containing composite oxides of Working Example 1, Working Example 2, Working Example 8, Comparative Example 1 and Comparative Example 2.

[Document name] Drawings

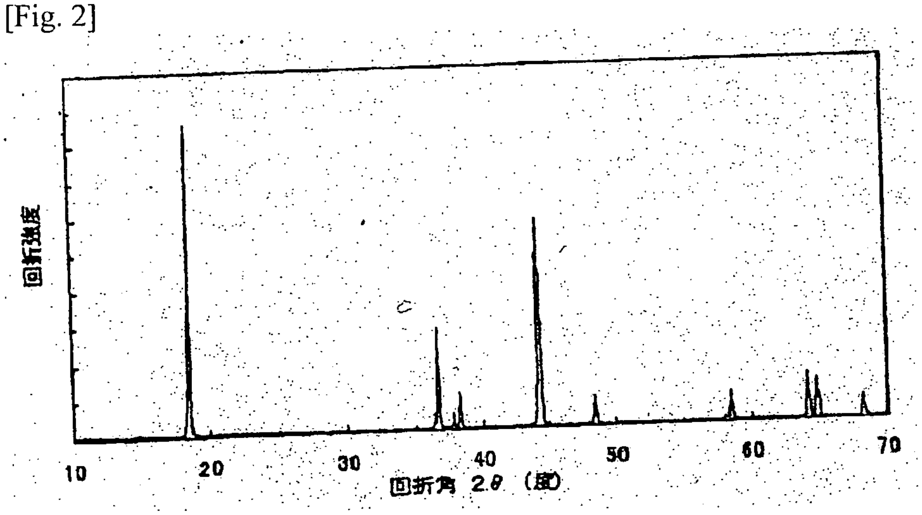
[Fig. 1]



Vertical axis: Diffraction intensity

Horizontal axis: Diffraction angle 2θ (degrees)

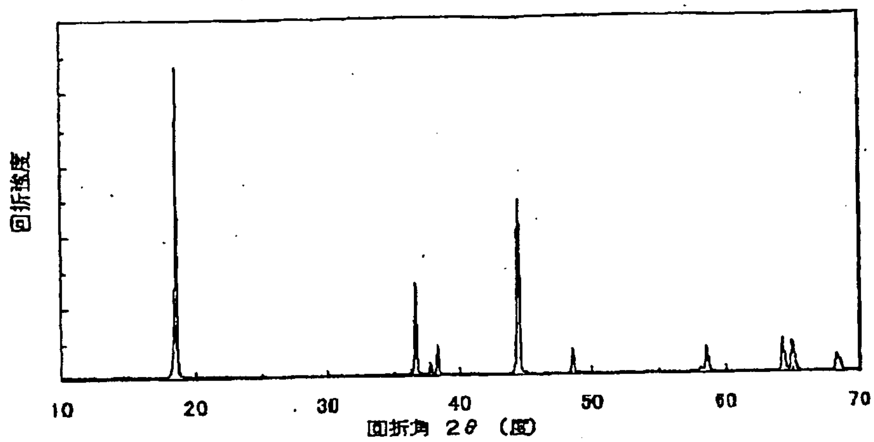
[Fig. 2]



Vertical axis: Diffraction intensity

Horizontal axis: Diffraction angle 2θ (degrees)

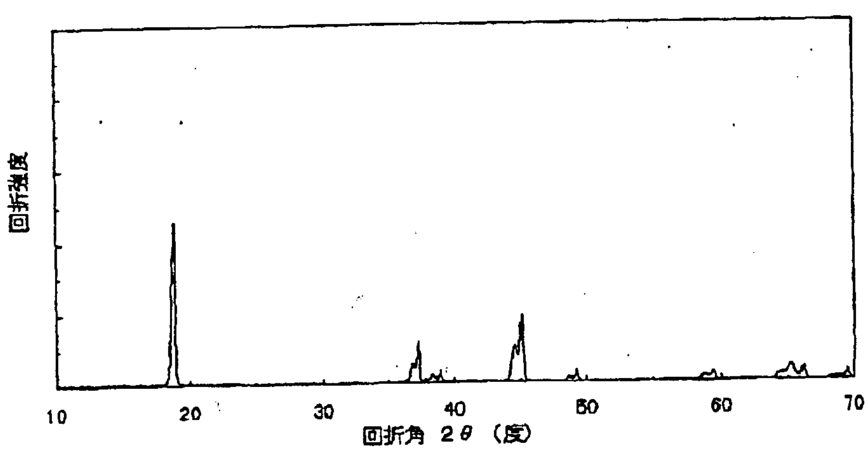
[Fig. 3]



Vertical axis: Diffraction intensity

Horizontal axis: Diffraction angle 2θ (degrees)

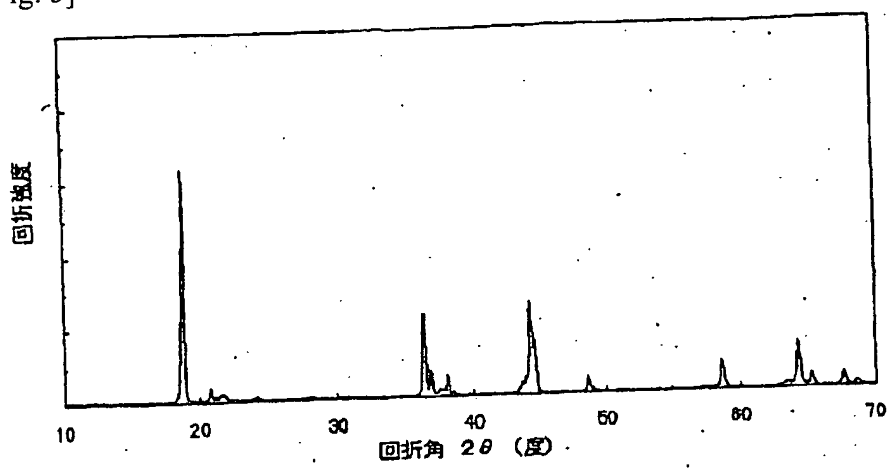
[Fig. 4]



Vertical axis: Diffraction intensity

Horizontal axis: Diffraction angle 2θ (degrees)

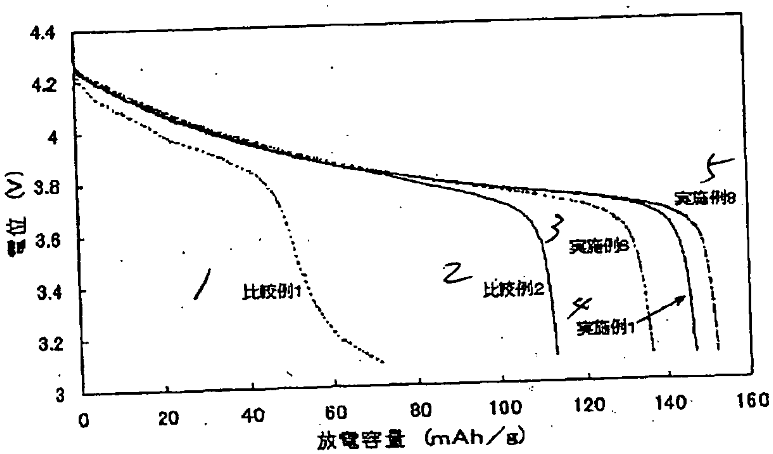
[Fig. 5]



Vertical axis: Diffraction intensity

Horizontal axis: Diffraction angle 2θ (degrees)

[Fig. 6]



Vertical axis: Potential (V)

Horizontal axis: Discharge capacity (mAh/g)

Key:

1 Comparative Example 1
2 Comparative Example 2
3 Working Example 6
4 Working Example 1
5 Working Example 8

[Document name] Abstract

[Abstract]

[Purpose] The purpose of the present invention is to produce a lithium-containing composite oxide having stable layer-like crystal structure, high-density and excellent reversibility of charge and discharge, and to produce a high capacity non-aqueous secondary cell having high durability using the above-mentioned as a positive electrode.

[Means of solution] Synthesis of a single phase composite oxide having a structure indicated by the general formula $Li_{1+x+\alpha}Ni_{(1-x-y+\delta)/2}Mn_{(1-x-y-\delta)/2}M_yO_2$ [Wherein, $0 \le x \le 0.05$, $-0.05 \le x+\alpha \le 0.05$, and $0 \le y \le 0.4$, and $-0.1 \le \delta \le 0.1$ (provided that $0 \le y \le 0.2$) or $-0.24 \le \delta \le 0.24$ (provided that $0.2 < y \le 0.4$), and M is one or more types of elements selected from a group comprising Ti, Cr, Fe, Co, Cu, Zn, Al, Ge, and Sn].

[Selected drawing] None

Additional Information on Applicant

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Address: 1-1-88 Ushitora, Ibaragi-shi, Osaka-fu

Name: Hitachi Maxell Co., Ltd.

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